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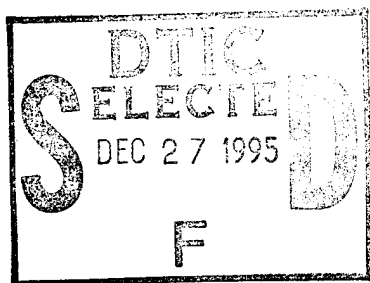
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13. Abstract (Maximum 200 words). The carbonate sediments from Fort Jefferson National Monument area are being studied for porewater geochemistry, mineralogy and microfabric in order to evaluate the effects of seafloor diagenesis to the sediment structure. Cementation is suggested at the depths of 120 cm and below by the increase in high-Mg/low-Mg calcite ratio determined by the Rietveld crystal structure refinement. More detailed mineralogy study and porewater geochemistry of deeper samples will possibly confirm this suggestion. Seafloor diagenesis may be significant at the depths where the effects of bioturbation and storm mixing do not reach.					
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**Geochemical, mineralogical and microstructural study of the seafloor
diagenesis of carbonate sediments in Fort Jefferson National Monument area**

by

Yoko Furukawa

Center for Marine Sciences
The University of Southern Mississippi
Stennis Space Center, MS 39529



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Denis Wiesenburg, Principal Investigator

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1. Introduction

Sediment microstructure is largely determined by chemical diagenesis and physical processes such as bioturbation and storm reworking in the carbonate sediments of Fort Jefferson National Monument area, west of Key West, Florida. Consequently, understanding of the extent of chemical diagenesis and physical reworking is essential in order to understand the sediment structure as well as the geophysical and geoacoustic properties affected by the sediment structure. The present study investigates the mineralogy, porewater geochemistry, and sediment microstructure of a number of box and gravity cores from the study area in order to quantify the extent of chemical diagenesis.

This study, funded by the Naval Research Laboratory (NRL), is a part of the large research program managed by the Office of Naval Research (ONR) called Coastal Benthic Boundary Layer Special Research Program (CBBL-SRP). The objective of the CBBL-SRP is to characterize and model benthic boundary layer processes and the impact such processes cause on seafloor properties that affect shallow-water naval operation (Richardson, 1995). The present study investigates the chemical diagenesis on an attempt to understand the relationship between the sediment structure and processes that form the structure, chemical diagenesis, sedimentation and physical reworking.

2. Methods

The author participated in the CBBL-SRP Key West Campaign that was conducted in the area of carbonate sediments near Dry Tortugas (Fort Jefferson National Monument) and Marquesas Keys, west of Key West, Florida in the Gulf of Mexico. The cruise was conducted on board the German research vessel *WFS Planet* in February 1995. The results reported in this paper are from the Dry Tortugas sediments, as the calmer weather conditions of Dry Tortugas allowed the sampling effort to be more thorough and extensive.

Sediment samples were obtained from the upper 2 m using box cores and gravity cores. Porewater samples were obtained from the upper 30 cm of sediment by using Jahnke-type porewater squeezers (Jahnke, 1988) to subsample the box core samples. Abundant organisms such as worms and shrimps which are known to cause significant biological mixing of surface sediments were found in the box cores. Porewater samples were collected and processed on board *WFS Planet*. Sediment samples from box cores were collected by Dennis Lavoie of NRL and the author. Sediment samples from gravity cores were collected by Dawn Lavoie of NRL on board *R/V Pelican* during the CBBL-SRP Key West Campaign.

Porewater samples were drawn from Jahnke-type squeezer that prevented samples from exposure to air and subsequent oxidation. Porewater samples were analyzed for intermediate inorganic sulfur species and total inorganic reduced sulfur species using iodometric titration (Grasshoff, 1983; Fonselius, 1983) within 10 minutes of the completion of sampling. Major and minor cation concentrations were determined using inductively coupled plasma spectroscopy

(ICP) by Chuck Holmes at US Geological Survey (USGS) Denver Office. The porewater samples were also analyzed for pH within 10 minutes of sampling.

Sediments from both box cores and gravity cores were sampled for the study of mineralogy and microfabric. Mineralogy is studied using X-ray powder diffraction (XRD) and the subsequent Rietveld crystal structure refinement (Rietveld, 1969; Young et al., 1994). The Rietveld method of refinement is capable of quantifying the calcium carbonate phases with various Mg contents (Bish and Post 1993). Although the accuracy of absolute values determined by this method is still debated (Mansour et al., 1995), the relative quantities of aragonite, high-Mg calcite and low-Mg calcite determined by the Rietveld method can be compared between samples (Reid et al., 1993). The Rietveld method also provides the cell constants of high-Mg and low-Mg calcites from which Mg contents can be calculated using the existing correlation curve (Goldsmith et al., 1958). Microfabric is studied using petrographic microscope, a scanning electron microscope (SEM) and a transmission electron microscope (TEM). Samples for petrographic microscope and SEM examinations were taken from gravity cores using 1 inch diameter plastic syringes as mini-corers and air dried in a low temperature (30°C) oven. These samples were subsequently embedded in Spurr resin and polished. The TEM samples were taken from subcores of box cores using the drinking straw mini-corers and subsequent fluid exchange embedding method (Lavoie et al., 1995).

3. Results

The results of porewater analyses are shown in Figures 1, 2, and 3. Within upper 30 cm of the sediments, the concentrations of Ca^{2+} and Mg^{2+} normalized to the concentration of Na^+ remain nearly constant (Figure 1). The porewater sulfur speciation (Figure 2) indicates that the aqueous inorganic sulfur species with intermediate oxidation states exist in the sediment porewater. Intermediate sulfur species here includes aqueous inorganic sulfur species with oxidation states between that of sulfide (-2) and sulfate (+6), namely, sulfite and thiosulfate. The intermediate species are the evidence of the sulfide re-oxidation because the bacterial reduction of seawater sulfate results in the direct production of sulfide and does not produces the intermediate species. The reoxidation is most extensive at the depths between 7 cm and 11 cm where most of the reduced sulfide is intermediate species. The porewater pH slightly increases at depth (Figure 3).

The results of the XRD and subsequent Rietveld crystal structure refinement are shown in Figures 4, 5, and 6. The sediments are the mixture of aragonite, high-Mg calcite, low-Mg calcite, and non-carbonate fraction that is dominated by quartz. Whereas the ratio of aragonite to total calcite remains nearly constant throughout the gravity core sampling depths (Figure 4), the ratio of high-Mg calcite to low-Mg calcite increases at depths (Figure 6). The compositions of both high-Mg calcite (~12.5% MgCO_3) and low-Mg calcite (~1.5% MgCO_3) stay nearly constant throughout the sampling depths (Figure 5).

The microfabric study by petrographic microscope, SEM, and TEM revealed that the sediments from the study area are bimodal in grain size with grains of mostly green algae (*Halimeda*) plates and fine-grained matrix. The TEM photographs of the sediments near the

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sediment-water interface (Figure 7) indicate that the matrix is composed of particles of many different morphologies including the aragonite needles similar to the aragonite needles within the *Halimeda* plates.

The schematic representation of one of the gravity cores is shown in Figure 8. The very shelly layers at 100 cm below the sediment water interface and again at 165 cm are possibly the remnants of storm-sorted layers.

4. Discussion

In carbonate sediments, a shift in $[Ca^{2+}]$ or $[Mg^{2+}]$ may indicate the dissolution or precipitation of calcium carbonate phases due to the seafloor diagenesis. As shown in Figure 1, such shift was not observed in the upper 30 cm of the sediments in the study area. However, because of the reworking due to bioturbation suggested by the presence of organisms and storm mixing suggested by the very shelly layers (Figure 8), the lateral mixing of porewater must be extensive in the study area. Therefore, $[Ca^{2+}]$ and $[Mg^{2+}]$ can not be used as indicators of the extent of seafloor diagenesis, at least within the upper part of the sediments where storm mixing and bioturbation are extensive. As the Rietveld refinement suggested, the effect of bioturbation and storm mixing may not reach depths below 120 cm and cementation may be occurring. Therefore, $[Ca^{2+}]$ and $[Mg^{2+}]$ may show the expected shift due to seafloor diagenesis at deeper depths.

The existence of intermediate sulfur species (Figure 2) indicates the ongoing oxidation of aqueous sulfide. The oxidation of aqueous sulfide leads to the production of a proton as follows:



and then carbonate can be dissolved as follows:



Therefore, the dissolution of carbonate minerals may be possible in the study site due to the ongoing reoxidation of aqueous sulfide. However, the pH measurement (Figure 3) indicates that the decrease of pH expected from the reoxidation especially at the depths between 7 cm and 11 cm does not occur. Therefore, the reoxidation of aqueous sulfide can not be a major mechanism of seafloor diagenesis of the bulk sediments in the study area. It may be important within microenvironment such as the area of extensive bioturbation where porewater may be locally more oxygenated than the bulk porewater.

The increase in high-Mg/low-Mg calcite ratio within the bulk sediments at depths (Figure 6) may be the result of cementation. Most cement in shallow water sediments is either high-Mg calcite or aragonite (Bathurst, 1975). Because the effect of cementation should be more notable within the matrix than around the surface of grains due to the surface area difference, the

comparison of matrix mineralogy vs. grain mineralogy may clarify the reason for the observed shift. If the observed shift in high-Mg/low-Mg calcite ratio comes from the cementation, the matrix mineralogy would show the same shift whereas the grain mineralogy remains constant. If the shift is from the difference in depositional environment that results in more high-Mg calcite grains (e.g., red algae and benthic foraminefera) at depths, both matrix mineralogy and grain mineralogy would show the shift. If the shift is indeed determined to be due to the cementation, the lack of shift within the upper 120 cm of the sediments may be due to the physical reworking and/or lack of cementation. The ^{210}Pb analysis should provide the thickness of the mixing layer. The cementation may become significant right below the mixing layer, or may not be detectable by mineralogy, microfabric or porewater chemistry until the sediment is buried without mixing for a long period of time.

The coexistence of fresh *Halimeda* plates and aragonite-needle matrix (Figure 7) may suggest extensive reworking in the study area. The aragonite needles in the matrix may be the remnants of old, abraded *Halimeda* plates that were reworked and mixed with fresh plates. The presence of the possible storm layers (Figure 8) also supports the idea that physical mixing is extensive in the study area. Further microfabric study is needed for samples from all depths.

5. Further study

The XRD on matrix and grain fractions has been completed. The results of Rietveld refinement should be ready by the Geological Society of America meeting in November 6-9, 1995. Microfabric study, especially TEM study, is planned for samples from gravity cores in order to visualize the possible diagenetic features and effect of physical reworking. Another cruise to the study area is being planned for the collection of porewater from gravity cores. As the possible cementation occurs below 120 cm, it is important to obtain $[\text{Mg}^{2+}]$ and $[\text{Ca}^{2+}]$ data from those depths. ^{210}Pb dating on sediments down to 30 cm deep is being carried out at SUNY Stony Brook by Chuck Nittrouer and coworkers and should be available soon.

6. Conclusions

Whereas the physical mixing processes are extensive in obscuring the evidence for seafloor chemical diagenesis, the chemical alteration may be seen in terms of matrix mineralogy change at the depths where the effect of physical mixing has not reached for a certain length of time. Further deeper (120 cm and below) study is required in order to quantify the extent of seafloor diagenesis by using matrix fraction mineralogy and porewater chemistry.

7. References

- Bathurst, R. G. C. (1975) *Carbonate sediments and their diagenesis Second Enlarged Edition*. Developments in Sedimentology Vol. 12. Elsevier.

- Bish, D. L. and Post, J. E. (1993) Quantitative mineralogical analysis using the Rietveld full-pattern fitting method. *Amer. Mineral.* **78**, 932-940.
- Fonselius, S. H. (1983) Determination of hydrogen sulphide. In *Methods of Seawater Analysis* (ed. K. Grasshoff et al.), 2nd rev., Chap. 6. Weinheim: Verlag Chemie.
- Goldsmith, J. R. and Graf, D. L. (1958) Relation between lattice constants and composition of the Ca-Mg carbonates. *Amer. Mineral.* **43**, 84-101.
- Grasshoff, K. (1983) Determination of thiosulphate. In *Methods of Seawater Analysis* (ed. K. Grasshoff et al.), 2nd rev., Chap. 5. Weinheim: Verlag Chemie.
- Jahnke R. A. (1988) A simple, reliable, and inexpensive pore-water sampler. *Limnol. Oceanogr.* **33**, 483-487.
- Lavoie, D. M., Baerwald, R. J., Hulbert, M. H. and Bennett, R. H. (1995) A drinking straw minicorer for sediments. *J. Sed. Res. Sec. A: Sed. Petrol. and Proc.* (Submitted)
- Mansour, A. M., Piller, W. E., and Lengauer, C. L. (1995) Quantitative mineralogical analyses of carbonate rich sediments by X-ray powder diffraction. *Powder Diffraction* **10**, 112-116.
- Richardson, M. (1995) Introduction. *Key West Campaign Cruise Reports* (compiled M. D. Richardson and L. Cole), Chap. 1. Naval Research Laboratory.
- Reid, R. P., MacIntyre, I. G. and Post, J. E. (1992) Micritized skeletal grains in northern Belize Lagoon: A major source of Mg-calcite mud. *J. Sed. Petrol.* **62**, 145-156.
- Rietveld, H. M. (1969) A profile refinement method for nuclear and magnetic structures. *J. Appl. Cryst.* **2**, 65-71.
- Young, R. A., Sakthivel, A., Moss, T. S., and Pavia-Santos, C. O. (1994) User's guide to program DBWS9411 for Rietveld analysis of X-ray and neutron powder diffraction patterns with a 'PC' and various other computers. School of Physics, Georgia Institute of Technology, Atlanta, Georgia.

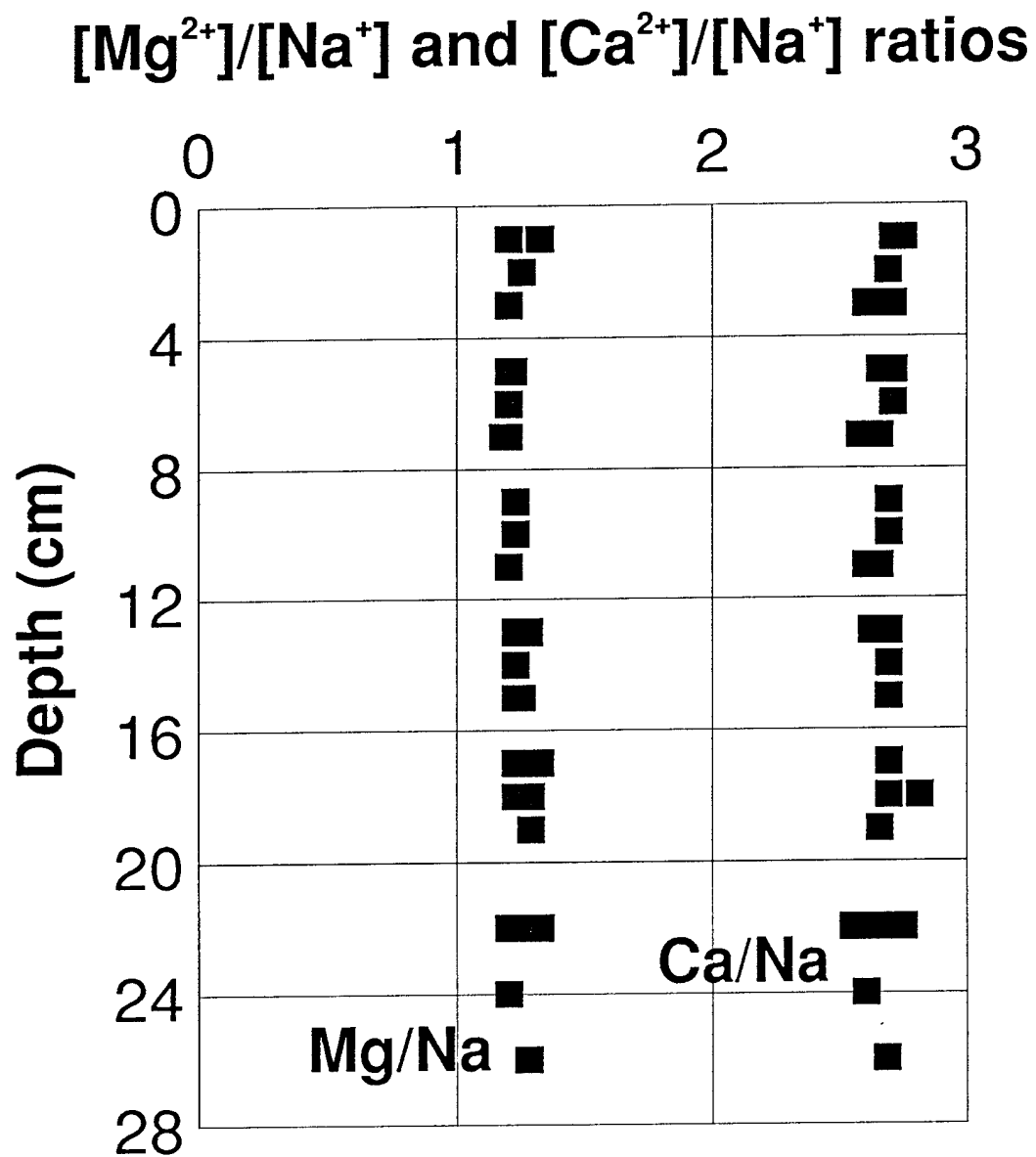


Figure 1. Porewater [Mg²⁺]/[Na⁺] and [Ca²⁺]/[Na⁺] ratios of samples from three box cores (KW-PL-BC-141, 165, 194) and from a diver core (KW-PL-DC-179). The ratios remain nearly constant through the sampling depths.

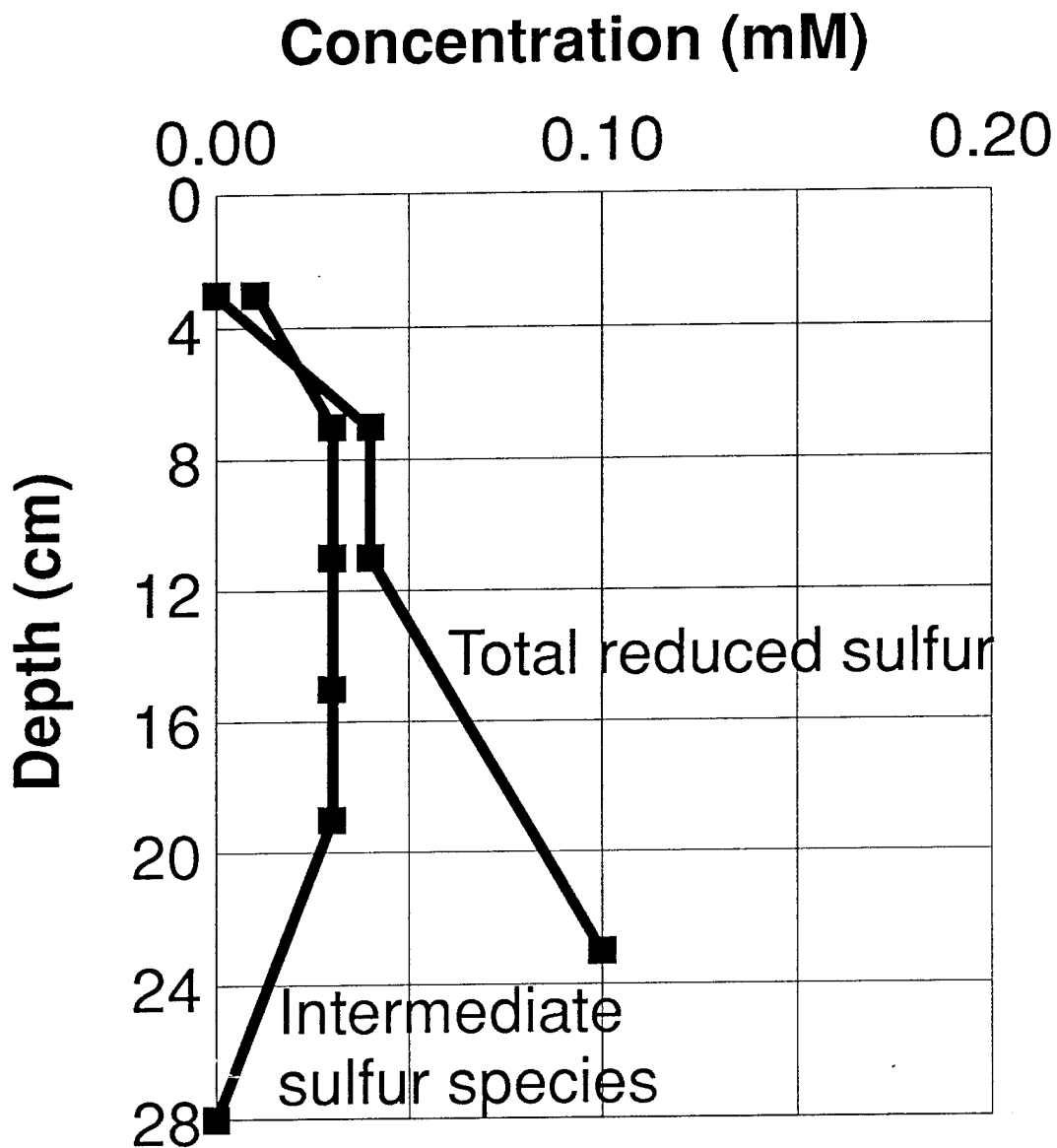


Figure 2. Porewater sulfur speciation of samples from a box core (KW-PL-BC-194). Total reduced sulfur includes sulfide (H_2S and HS^-), polysulfides (S_x^{2-}), thiosulfate ($\text{S}_2\text{O}_3^{2-}$), and sulfite (SO_3^{2-}). Intermediate sulfur species include thiosulfate and sulfite. At the depths between 7 cm and 11 cm, most reduced sulfur is in the form of intermediate species.

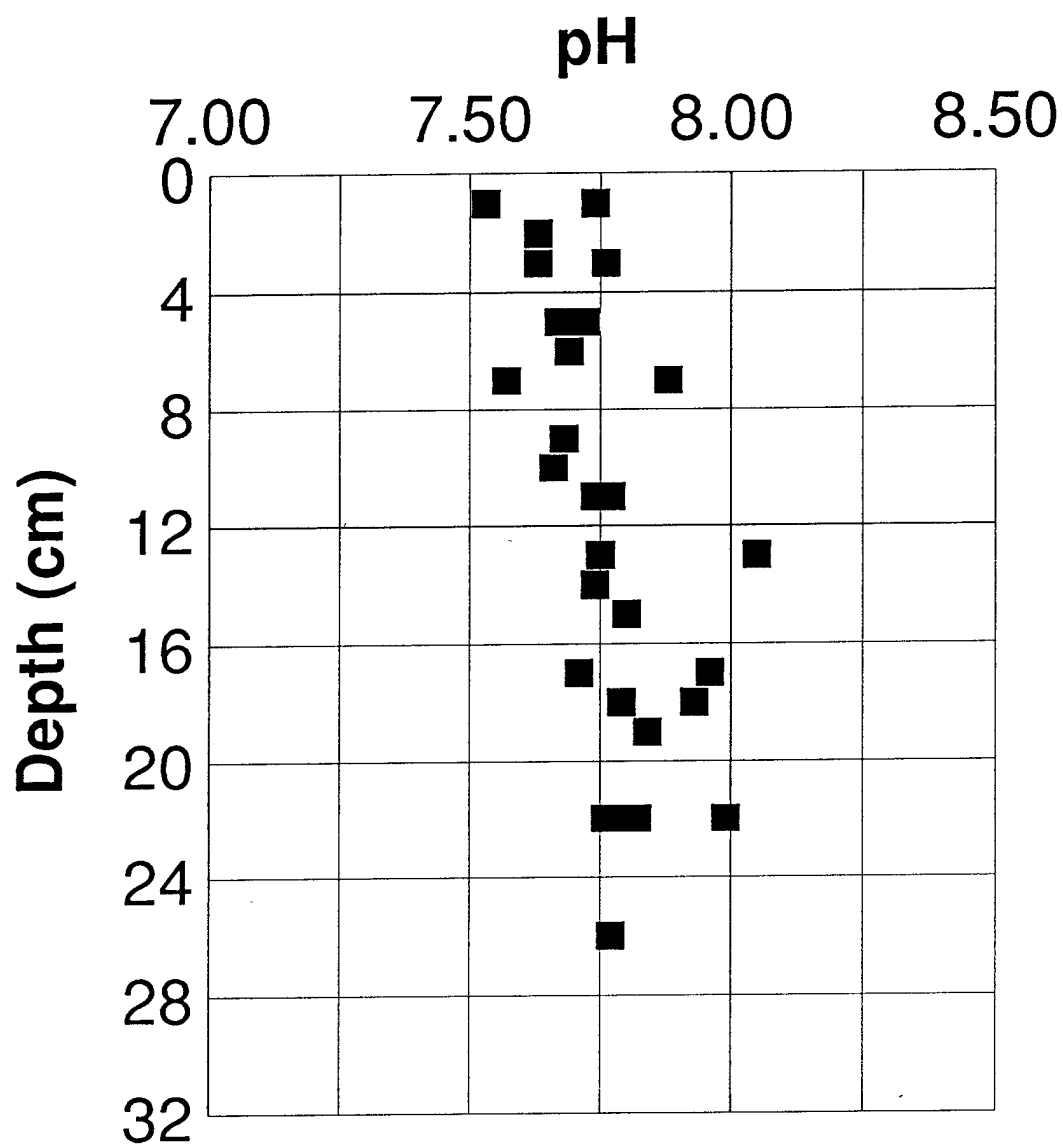


Figure 3. Porewater pH of samples from three box cores (KW-PL-BC-141, 165, 194) and a diver core (KW-PL-DC-179). The pH increases slightly with depth.

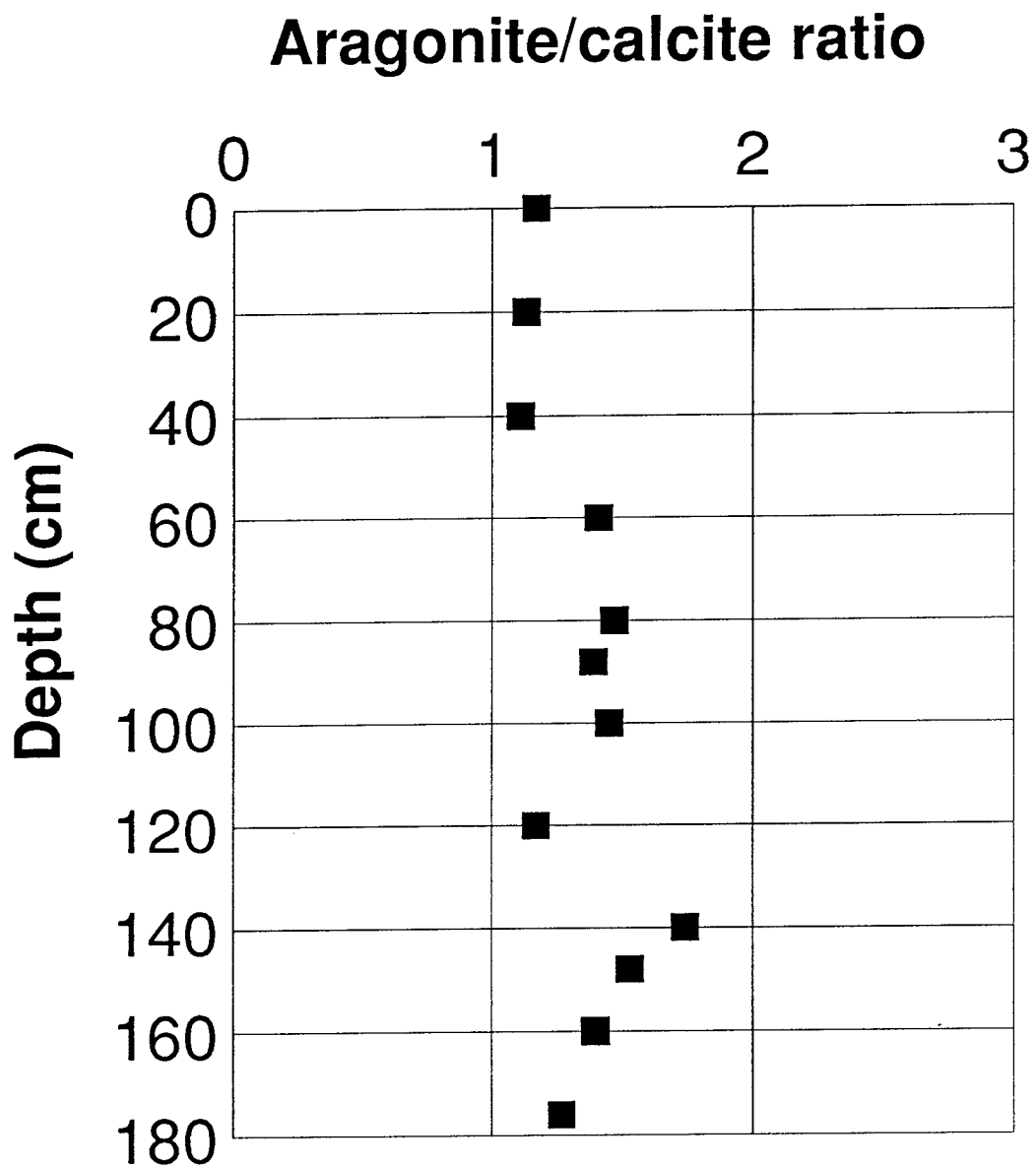


Figure 4. Aragonite/total calcite ratio determined by the XRD and subsequent Rietveld method for samples from a gravity core (KW-PL-GC-147). The ratio remains nearly constant through the sampling depths.

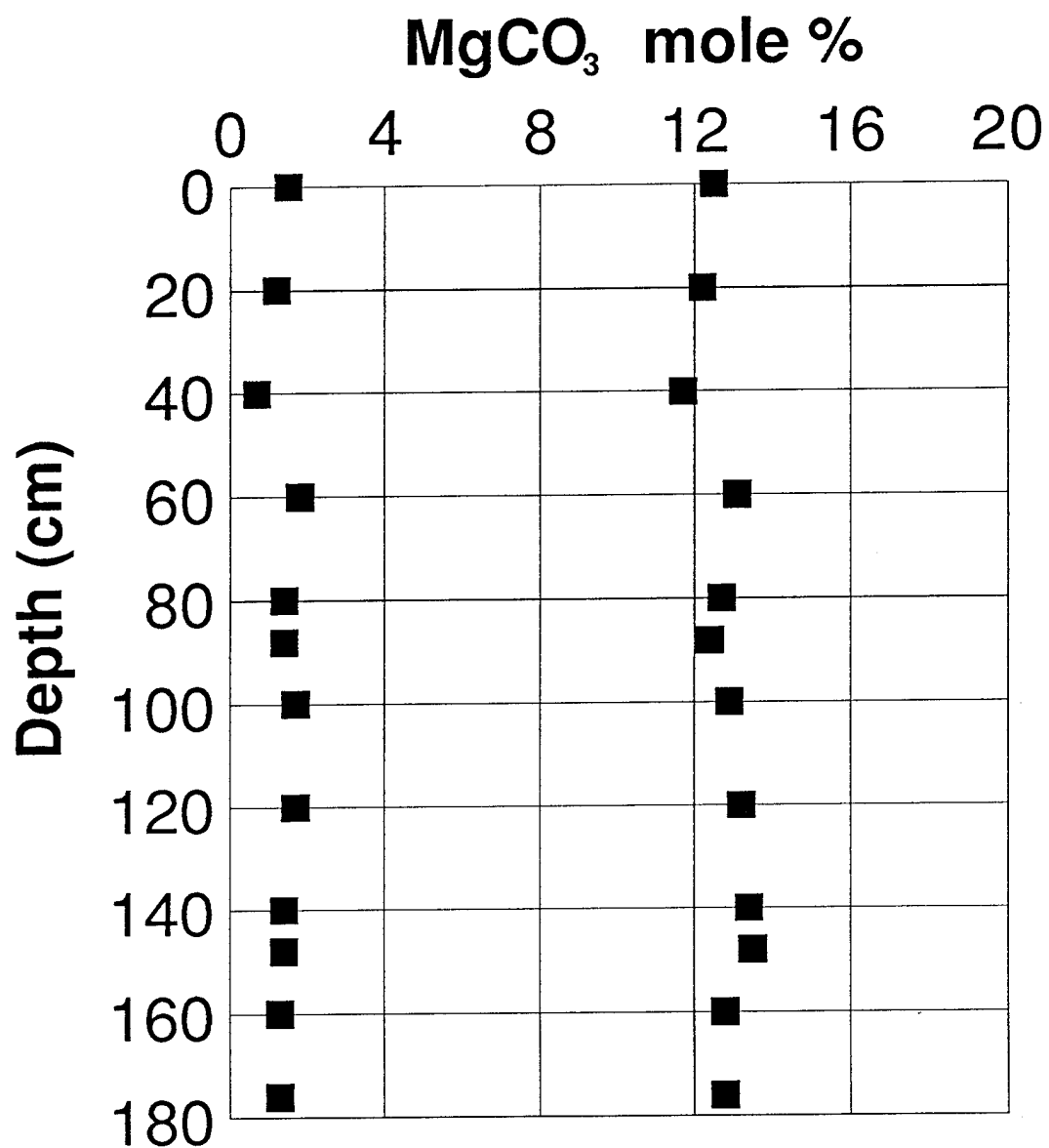


Figure 5. Calcite compositions determined by the XRD and subsequent Rietveld method. Samples are from a gravity core (KW-PE-GC-147). The compositions of both high-Mg and low-Mg calcites are nearly constant through the sampling depths.

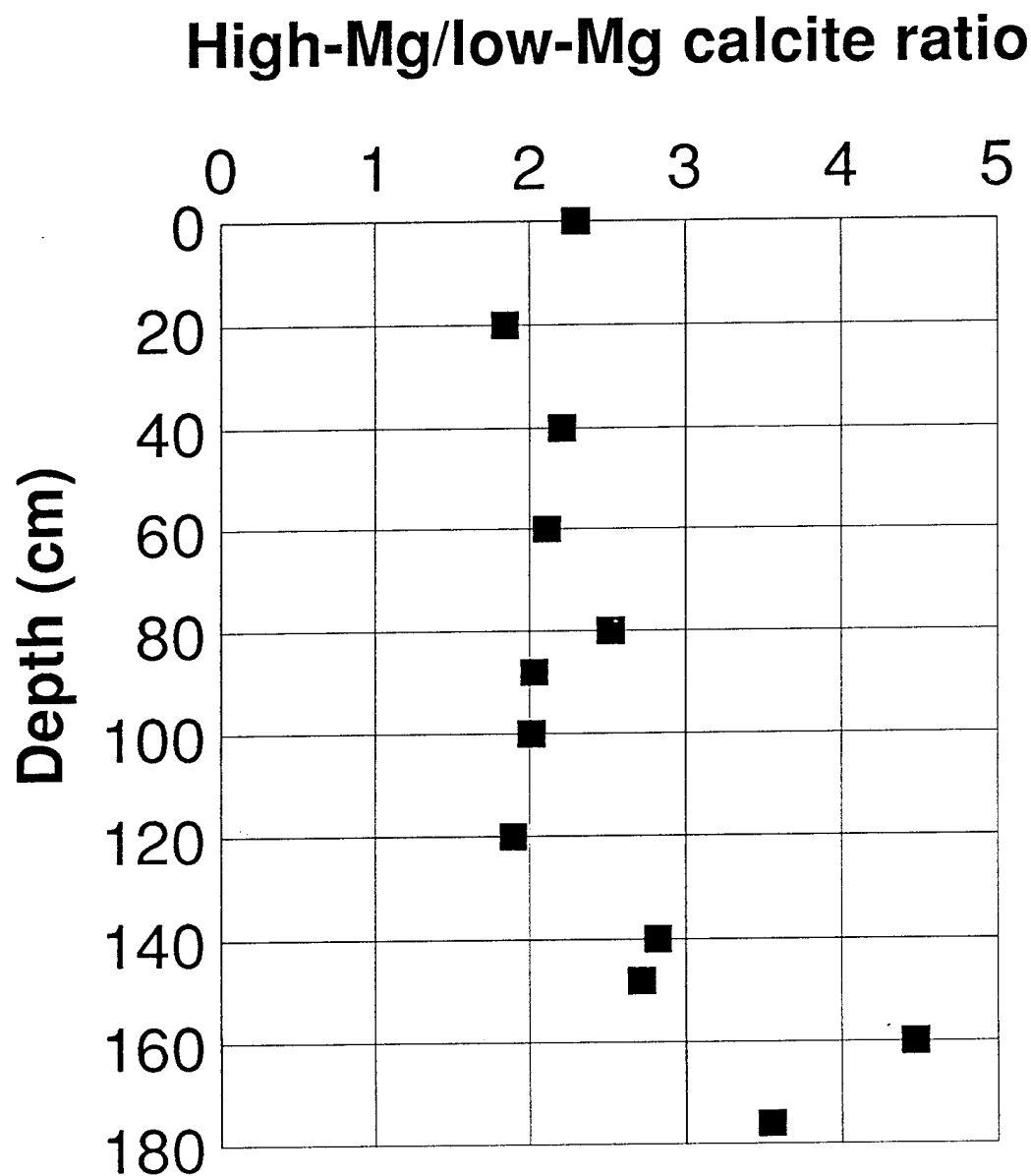


Figure 6. High-Mg/low-Mg calcite ratio determined by the XRD and subsequent Rietveld method. The ratio increases at the depth of 120 cm below sediment-water interface and below.

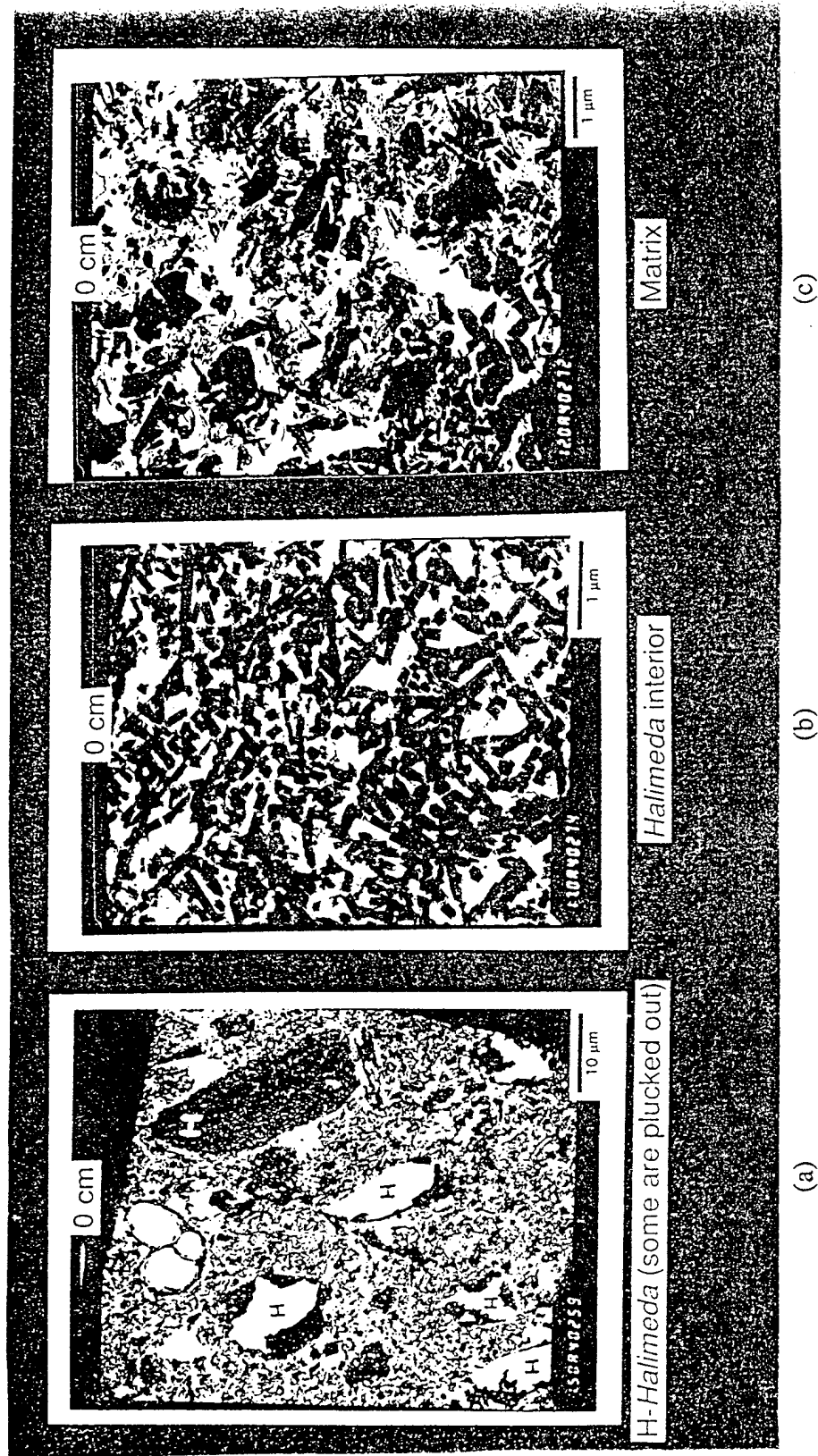


Figure 7. TEM images of a sample from the box core KW-PE-GC-194. (a) Grains of *Halimeda* (some are plucked out during the sample preparation) and the fine-grained matrix. (b) A magnified image of the *Halimeda* interior displaying the internal structure exclusively composed of aragonite needles. (c) A magnified image of the matrix showing the particles of many different morphologies.

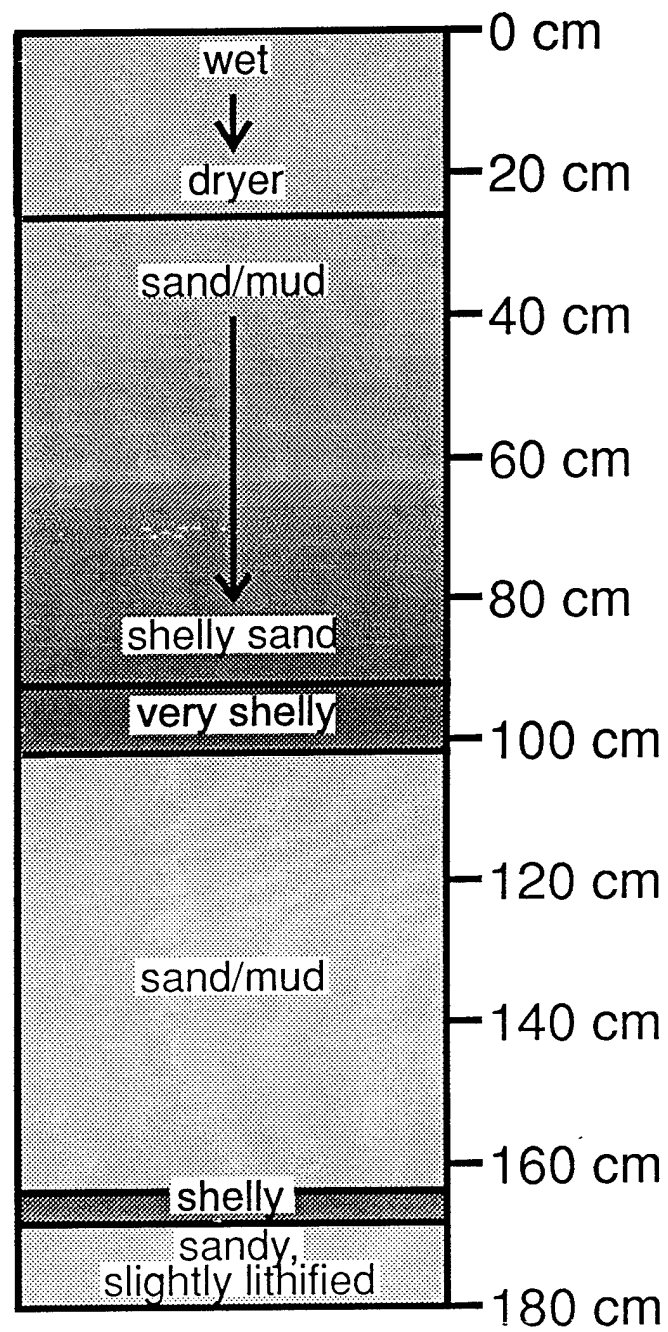


Figure 8. Lithology observed in the gravity core KW-PE-GC-147.